



Convention Dates
(United States of America)

March 20, 1943.
May 6, 1943.

Corresponding Applications
in United Kingdom

No. 2865/44 } dated Feb. 16, 1944.
No. 2866/44 }

(One Complete Specification left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1942.)

Specification Accepted: April 29, 1947.

COMPLETE SPECIFICATION

Improvements in or relating to Alcoholysis of Fatty Glycerides

We, COLGATE-PALMOLIVE-PETT COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 105, Hudson Street, Jersey City, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a process for removing desired reaction products from reaction mixtures obtained by the alcoholysis of fatty glycerides and, more particularly, to a process for separately recovering glycerine and alkyl esters or esters of polyhydric alcohols and unreacted alcohol in a substantially pure state from said mixtures.

A fat or fatty oil can be reacted with an alcohol in the presence of an alcoholysis catalyst to produce glycerine and alcohol esters of fatty acids. The reaction mixture may contain triglycerides, mono- and di-glycerides and other fatty acid mono esters of polyhydric alcohols, fatty acid esters of monohydric alcohols, glycerine and excess alcohol, the proportions of the various ingredients varying with the extent of the reaction. According to the prior art, it was believed to be impossible to distill such a reaction mixture containing mono- and/or di-glycerides without a back reaction occurring whereby the partial esters are converted to glycerine and triglycerides. Moreover, the prior art taught that the heating of an alcoholysis reaction mixture comprising alkyl esters and glycerine, with or without the presence of mono- and di-glycerides, would result in reversion to glycerides and alcohol, especially under the continuous removal of the alcohol by volatilisation.

Since, by the processes employed by the prior art, glycerine was not readily separated from the fatty acid alkyl esters,

i.e. there being no sharp separation of the components into two layers separate processing of each layer was required. The difficulties of the separation method were increased when using ethyl or other alcohols higher than methyl for the alcoholysis, as a separation of glycerine from esters was frequently not immediately obtainable in such cases, separate layers not being formed. Excess alcohol and catalyst were washed out with water to effect a separation, such washing operation being a tedious and uneconomic procedure. Moreover, in washing with water, the resulting dilution of the glycerine required a concentration step, and the recovered unreacted alcohol had to be dehydrated before reuse.

Although the mechanism of alcoholysis of fatty glycerides is not completely understood as yet, research investigations now indicate that, when using alkaline catalysts, the extent of alcoholysis of fatty glycerides, i.e. the yield of fatty acid esters and glycerine depends upon the rate of interchange of glyceryl radicals with the radicals of the alcohol employed in the alcoholysis as against the rate of saponification by free alkali of the fatty acid esters formed and of the still unreacted or partially reacted glycerides. It is therefore advantageous to provide a low rate of soap formation as compared with the rate of alcoholysis, and the soap content of the reaction mixture increases with an increase in the amount of alkaline catalyst employed, with an increase in temperature, with an increase in the length of reaction time, and with an increase in the water content. An increased excess of alcohol, however, permits a reduction in the total amount of alkaline catalyst needed to produce a maximum yield of esters.

In our co-pending application No. 17058—9 of 1943 (Serial No. 587,524) an alcoholysis process using an alkaline catalyst is described and claimed the said

[Price 1s. 4d.]

process involving the volatilisation of unreacted alcohol from the reaction products, one feature of the invention comprising acidification of the residual liquid, after volatilising the alcohol with an acid stronger than the fatty acid of the glyceride.

We have now found that in alcoholysis of fatty glycerides both with alkaline and acid catalysts the neutralisation or inhibition of the catalyst prior to the removal of the unreacted alcohol not only facilitates the later separation of glycerine but also precludes back reaction during the distillation of the alcohol.

Thus, following the neutralisation or inhibition of the catalyst according to our invention, mixtures of glycerine with monohydric alcohol esters of fatty acids can be distilled together without interaction, and similarly excess glycerine and the monoglycerides may be distilled from the reaction products of the glycerine alcoholysis of fatty esters, without substantial chemical degradation or reversion. Di-glycerides are also unchanged under the same conditions.

Accordingly in an alcoholysis reaction between a fatty glyceride and an alcohol in the presence of an alcoholysis catalyst in which the alcohol reaction component is a monohydric or polyhydric alcohol, the invention comprises removing the influence of the catalyst by the addition of a neutralising agent before removing unreacted alcohol and before recovering the reaction products from the liquid reaction mixture.

The influence of the catalyst is removed by bringing the pH sufficiently near the neutral point to render the catalyst inert, i.e. to a pH of 3-10 as hereinafter described.

The alcoholysis of waxes of natural origin (which are known to consist essentially of esters of high molecular weight carboxylic acids and high molecular weight monohydric alcohols) in the presence of an alcoholysis catalyst has been proposed hitherto and in carrying out the said alcoholysis it was proposed to neutralise the catalyst prior to volatilisation of unreacted alcohol from the reaction mixture.

According to one form of the invention alkyl esters and glycerine are recovered after substantial neutralisation of the alcoholysis catalyst, by distilling them together from the reaction body formed by reacting a fatty acid glyceride with a lower aliphatic alcohol.

According to another feature of the invention a mixture resulting from the reaction in the presence of an alcoholysis catalyst of the fatty glyceride with an

alcohol and containing fatty acid partial esters of a polyhydric alcohol, is substantially neutralised to remove the influence of the catalyst. The fatty acid partial esters of the polyhydric alcohol are then separated from other ingredients of the mixture by distillation without substantial reversion.

The fatty glycerides treated by the process of the invention may be any of the natural products such as the fats or fatty oils suitable for employment by the soap-making art in any of the processes heretofore known or artificial fatty glycerides, the fatty acids in each case having about eight to about twenty-six, and preferably about twelve to about twenty, carbon atoms per molecule. These esters include coconut oil, palm oil, olive oil, cottonseed oil, soya bean oil, corn oil, tung oil, tallow, whale and fish oils. Although it is better to employ a refined oil containing substantially no moisture, small amounts of water can be tolerated when carrying out the alcoholysis with the lower alcohols, such as methyl or ethyl alcohol and especially methanol. Similarly, where acid alcoholysis is employed or where, in alkaline alcoholysis, acidification of the reaction mixture for destruction of the alkaline catalyst is contemplated, free fatty acid may be present in the fatty material in the proportion of 10 to 20% by weight or even higher.

In carrying out the alcoholysis for the production of alkyl esters, primary alcohols, having a boiling-point in the presence of excess water of lower than 100° C. at atmospheric pressure, are preferably employed. Thus alcohols satisfactory for use in forming esters with the fatty acid components of the glycerides treated include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, secondary butyl alcohol, tertiary butyl alcohol, and the amyl alcohols. Preferably a saturated aliphatic monohydric alcohol having one to about six carbon atoms per molecule is employed. While any proportions of fatty material and alcohol may be used, it is preferred to employ an amount of alcohol at least about 50% in excess of the calculated theoretical amount necessary for alcoholysis of the particular glycerides treated, and particularly satisfactory results have been obtained when using an excess of at least three to five times the stoichiometric amount required.

In carrying out the alcoholysis for the production of partial esters of polyhydric alcohols, either a monohydric or a polyhydric alcohol may be used. Short-chain aliphatic polyhydric alcohols are preferably employed, particularly the saturated

alcohols and especially the lower polyhydric alcohols having two to about six carbon atoms per molecule. Thus, alcohols satisfactory for use in forming esters with the fatty acids or fatty acid components of the esters treated include glycerol and other trihydroxy alkanes, ethylene glycol, propylene glycol, trimethylene glycol, the amylene glycols, mannitol, sorbitol, and erythritol.

While any proportion of fatty material and alcohol may be used, depending upon the degree of radical interchange desired, it is preferred, when preparing monoesters, to employ an amount of polyhydric alcohol at least about 50% in excess of the calculated theoretical amount necessary for reaction with the particular esters treated, and particularly satisfactory results have been obtained when using an excess of at least three to ten times the stoichiometric amount required. On the other hand, when preparing di- or tri-esters, it is usually preferable to use no more than the stoichiometric amount. Thus, while two mols of glycerine are theoretically sufficient to convert all of one mol of a triglyceride to the monoglyceride, it has been found that, under these conditions, a large proportion of the resulting product is in the form of diglycerides. However, a proportion of about ten mols of glycerine to one of triglyceride gives a high yield of monoglycerides.

In carrying out the alcoholysis for the production of alkyl esters from a fatty glyceride the latter is contacted with the alcohol, preferably in large excess, in the presence of a small amount of the alcoholysis catalyst. The mixture may be kept at room temperature or may be heated during a period of a few minutes to obtain rapid alcoholysis. The reaction may be brought to the degree of completion desired in a single contacting of the materials, or the glycerides may be partially esterified with the monohydric alcohol in a first treatment to form a pool of partially reacted material containing monoglycerides and diglycerides, so that the reaction mixture is substantially homogeneous. Additional alcohol and/or alcoholysis catalyst either alone or with the fatty oil, can be added to this homogeneous mixture without immediately affecting the homogeneity, and the reaction may then be brought toward completion as described and claimed in our co-pending application No. 16959/43 (Serial No. 587,523).

When the reaction has reached the desired point, whether in a single contacting or in a series of steps, the catalyst is destroyed by neutralising the mixture or

by partially neutralising so as to form a mixture containing both free fatty acid and a fatty acid soap. The entire reaction mixture is then directly distilled first to remove the excess unreacted alcohol, and then, preferably under vacuum, to obtain a distillate comprising alkyl esters and glycerine, with or without the presence of fatty acids and/or partially reacted glycerides as determined by the operating conditions. This distillate readily separates into two phases, forming a lower glycerine layer and an upper layer comprising alkyl esters. The distillation residue may comprise soap and/or partially reacted glycerides and/or fatty acids, depending upon the operating conditions.

When removing alcohol, after rendering the catalyst inert, it may be desired to stop the distillation when substantially all of the excess alcohol has been removed, and then the glycerine and ester layers may be separated without (or before) distilling them. Since the distillation residue contains substantially no alcohol as a common solvent for glycerine and alkyl esters, a separation usually results. However, the codistillation of glycerine with fatty esters permits the use of a single reaction and at the same time reduces the still for the two separate products of the temperature of distillation for both, since the azeotropic codistillation which is obtained gives a lower boiling-point for the mixture than for either of the separate components thereof. In this way, the consumption of heat is less, and products are obtained which are less degraded by high temperature exposure.

In another modification, the reaction mixture after substantial neutralisation can be settled to separate a glycerine layer, which is withdrawn. The upper layer containing some glycerine, excess alcohol and alkyl esters, as well as fatty acids and/or mono- and/or di-glycerides if present, is then distilled, first at atmospheric pressure to remove the alcohol and then under vacuum to give a distillate which separates on standing into a glycerine layer and a layer containing alkyl esters, together with partially reacted glycerides if present. As in the modification described above, the distillation of the upper layer can be stopped when substantially all unreacted alcohol is removed thereby, whereafter another glycerine layer can be withdrawn. Since substantially all of the glycerine held in the upper layer is removed by this procedure, the resulting upper layer can be used without further distillation.

In preparing fatty acid monoglycerides, for example, a reaction be-

tween a triglyceride and glycerine may be carried out in the presence of either an alkaline or an acid alcoholysis catalyst. It has now been found that, if no trace of the alcoholysis catalyst remains after the reaction or if any catalyst present after the reaction is inhibited by substantial neutralisation, the reaction mixture may be heated to volatilise excess glycerine, and the mono-glycerides may be distilled, without substantial chemical degradation or reversion. Monoglycerides may be recovered in like manner from mixtures resulting from the alcoholysis, in the presence of a catalyst, of a triglyceride (and/or a diglyceride) with a lower alkyl alcohol.

In the preferred procedure for forming the reaction mixture, a fatty acid glyceride (whether naturally-occurring or synthetically produced) is contacted with a polyhydric alcohol, preferably in large excess, in the presence of a small amount of an alcoholysis catalyst. The mixture may be kept at ambient temperatures or may be heated during a period of a few minutes to obtain rapid alcoholysis. When the reaction has reached the desired point, whether in a single contacting or in a series of steps, the catalyst is destroyed by substantially neutralising the mixture. The entire reaction mixture is then directly distilled first to remove excess polyhydric alcohol, and then to obtain a distillate comprising polyhydric alcohol partial esters. If desired, only the excess polyhydric alcohol is removed by distillation, and the remainder of the mixture comprising polyhydric alcohol partial esters may be recovered for use without further purification.

In choosing an alcoholysis catalyst, an alkaline or an acidic catalyst may be employed. Among those which have been found suitable for use in the present process are sodium hydroxide, sodium methylate, sodium carbonate, barium oxide, lime, tetramethyl ammonium hydroxide, hydrochloric acid, trichloroacetic acid, phosphoric acid, sulphuric acid, aluminium chloride, boron fluoride, glycerine monoacid sulphate, alkyl sulphuric acids, and organic sulphonic acids. While it is possible to obtain good yields with proportions of alkaline catalyst up to about 0.30 mol per mol of fatty glycerides and higher, it is preferred to use large excesses of alcohol and to introduce relatively small amounts of catalyst, say of the order of about 0.03 mol to about 0.10 mol per mol of glycerides in order to reduce the amount of soap formed. With acidic catalysts, similar proportions are generally employed. A

convenient way of introducing the catalyst into the reaction mixture is in admixture with and, where practical, advantageously in solution in the alcohol employed. When the glyceride treated contains free fatty acid, sufficient alkaline catalyst may be added to provide an excess of alkali above that destroyed by the free fatty acid present. However, acid catalysts are particularly appropriate for use with oils containing a large proportion of free fatty acids, as the acids are esterified during the process.

In carrying out the alcoholysis according to this invention, the temperature may be regulated according to the materials used and the result desired. In general, when employing an alkaline catalyst, it is desirable to contact the fatty glyceride, alcohol and catalyst at about room temperature, particularly if small amounts of water are present, in order to avoid the possibility of excessive local saponification of the resulting esters. Such saponification removes the catalyst from the reaction body before the reactants have been thoroughly mixed and allowed to react. When the reactants are substantially anhydrous, they may be separately preheated to a desired reaction temperature and thoroughly mixed directly in a reaction coil or other vessel, whereby the reaction can be completed in an extremely short reaction time.

With either acid or alkaline catalyst, the reaction temperature may vary from about 40° C. to about 160° C. or higher and in preparing partial esters by alcoholysis with polyhydric alcohols from about 20° C. to 250° C., but in either case below the temperature of substantial degradation of the reactants or products formed. Where an alkaline catalyst is employed, the temperature of reaction should also be below the temperature of substantially complete removal of the alkaline catalyst by saponification of the resulting esters. In alcoholysis with either methanol or ethanol, it is preferred to maintain temperatures of about 80° C. to about 160° C., and temperatures of about 90° C. to about 130° C. have been found to give particularly satisfactory results. In alcoholysis with glycerine, it is preferred to maintain temperatures of about 150° C. to about 250° C., and temperatures of about 180° C. to about 200° C. have been found to give particularly satisfactory results. Similarly, when carrying out the alcoholysis with propylene glycol, temperatures of about 140° C. to about 220° C., and preferably about 160° C. to about 195° C., are advantageously maintained. In general, the operation may be carried

out as a batch, intermittent or continuous process, and at reduced pressures, at atmospheric pressure or at superatmospheric pressures, but it is preferred to provide a pressure in the reaction vessel or coil sufficient to maintain a liquid alcohol phase.

Upon completion of the reaction, the method for inhibiting the catalyst, whether alkaline or acid, is to neutralise the reaction mixture or to bring it to a pH of about 3 to about 10, or in the case of glycerine alcoholysis 5 to 8, and preferably in any case to a pH of about 5 to about 7, as indicated by the reading on the dial of a standard electronic pH meter using glass electrodes. The apparent pH of the mixture may be determined by indicators, a glass electrode or other suitable means. In neutralising a reaction mixture resulting from the alkaline alcoholysis of fatty glycerides, the neutralisation or change in pH is preferably carried out by the addition of an acid stronger than the fatty acids of the glyceride. A higher fatty acid or similarly weak acid may also be used in an amount in excess of that required for neutralising any free alkali present; the addition of a fatty acid causes the formation of a soap with the free alkali present, and any other acid as weak as a fatty acid, while neutralising the free alkali still in the mixture, is not strong enough to split the soap formed during the reaction by saponification of the fatty esters. In either case, the excess acid provided acts as an inhibitor of the catalytic effect of the soap present. "Neutral" soap (so-called) has otherwise been found to act as a catalyst for the glyceride-alcohol reaction at temperatures as low as about 140° C. and especially at temperatures above about 160° C. It is preferred to employ a strong mineral acid in the case of the polyhydric alcoholysis to produce partial esters.

Among the acids stronger than the fatty acids of the glycerides which have proved satisfactory for use in the present process are glacial acetic acid, hydrochloric acid, sulphuric acid, phosphoric acid, boric, sulphur dioxide and benzene sulphonic acid. It is preferred to employ a substantially non-aqueous acid to give an anhydrous alcohol suitable for reuse in the process without dehydration, as otherwise the excess alcohol recovered from the subsequent distillation step may contain a proportion of water. Where an aqueous acid is used, the amount of water introduced with the acid during acidification (that is, the concentration of the acid) is controlled so that the proportion of water in the recovered alcohol is relatively small.

When the reaction is carried out in the presence of an acid alcoholysis catalyst, the catalyst is inhibited upon completion of the reaction by introducing a material of an alkaline nature in strength and amount sufficient to bring the mixture to the desired pH but insufficient to leave any free alkali in the reaction mixture. Among the alkaline materials satisfactory for use in this process are caustic soda, soda ash, soap, sodium tetraborate and sodium acetate, and said materials are preferably added in substantially anhydrous condition. When employing a strong alkali, such as sodium hydroxide, an amount no more than sufficient to neutralise all of the acid catalyst is added; when using a relatively weakly alkaline material, such as the salts described, it is preferred to introduce a slight excess thereof. Thus, for example, the addition of a small excess of soap inhibits the acid catalyst by forming fatty acids, with a little soap still present in the mixture. In this manner, whether the reaction is catalysed by an acid or an alkaline catalyst, the reaction mixture is substantially the same after inhibition of the catalyst.

After eliminating the influence of the catalyst, the excess alcohol is preferably removed by distillation, heating the reaction mixture to a temperature sufficient to volatilise the alcohol but below the temperature of substantial decomposition or degradation of the products. It is preferred to distil the mixture at atmospheric pressure, although reduced pressures or superatmospheric pressures may also be used. In general, with coconut oil and oils having a mixture of glycerides of like molecular weight, temperatures below about 160° C. to about 200° C. give satisfactory results, and, with most glycerides, a temperature of about 110° C. to about 140° C. has been found to provide rapid removal of the lower alcohols.

When forming monoglycerides or glycolmonoesters from coconut oil or tallow or oils having a mixture of glycerides of like molecular weight, temperatures below about 150° C. at absolute pressures of about 3 to 4 mm. of mercury give satisfactory results.

After removal of the alcohols, the product is subjected to reduced pressures, say of the order of about 1 mm. to about 10 mm. of mercury absolute (although somewhat higher pressures can be employed), and is rapidly or flash distilled. The distillate may be fractionally condensed when there is a sufficiently wide difference in boiling-points between the glycerine and the particular esters formed or may be condensed jointly, whereupon

in the case of alcoholysis of glycerides to alkyl esters and glycerine it readily separates into two layers as aforesaid. The lower glycerine layer is withdrawn
 5 as a substantially pure, water-white and anhydrous liquid, and the upper layer containing alkyl esters, and in some cases incompletely reacted glycerides, is also removed as substantially colourless esters.
 10 With coconut oil as a starting material, monoesters of propylene glycol can be distilled at about 2 to 3 mm. of mercury at about 150° C. to about 160° C.; mono-glycerides of coconut oil distil at about
 15 185° C. to about 190° C. under an absolute pressure of about 1 mm. of mercury. With certain of the products contemplated, especially polyesters, it may be necessary or desirable to employ molecular distillation.

20 The following examples illustrate this invention, but it is not limited thereby.

EXAMPLE I.

215 parts by weight per minute of
 25 coconut oil is thoroughly mixed with 160 parts per minute of methyl alcohol and 1.6 parts per minute of sodium hydroxide during a period of some thirty seconds, the reactants being at 25° C. throughout
 30 the mixing. The mixture is run into a reaction coil having a holding time of approximately thirty seconds, and the temperature of the reactants is rapidly raised therein to about 130° C. Sufficient
 35 pressure is maintained within the coil to keep the methyl alcohol in the liquid state: The effluent from the coil passes, still under pressure, into a neutralising chamber where an alcoholic solution of
 40 glacial acetic acid at a rate of flow sufficient to give a pH of about 6 is thoroughly contacted with the reaction mixture. The mixture, thus substantially
 45 neutralised, is run into a preheater where its temperature is raised to about 145° C. The heated material is flashed into a vaporisation chamber at atmospheric
 50 pressure and then into a second chamber under a pressure of 100 mm. of mercury absolute. The excess alcohol is thereby volatilised and is withdrawn substantially
 55 anhydrous, whereby it can be reused in the process without dehydration. The remaining material passes to a vacuum still, where it is distilled under an absolute
 60 pressure of about 1 mm. of mercury. The distillate runs into a separation vessel, where it settles into two layers. The lower layer comprising glycerine is withdrawn, and the upper layer containing the methyl esters of coconut oil fatty
 acids overflows near the top of the separation vessel. Approximately 97.0% of the calculated theoretical yield is obtained.

EXAMPLE II.

295 pounds per minute of dry, refined
 sesame oil is run into a mixing vessel or
 contactor. Solid, anhydrous sodium
 hydroxide is dissolved in anhydrous
 methanol in the proportion of 1 part by
 70 weight of sodium hydroxide to 40 parts of methanol, and the alcoholic solution is run into the contactor at the rate of 65.6
 pounds per minute, (a rate which is
 75 approximately twice that theoretically necessary for alcoholysis of the sesame oil at the temperature of refluxing. The contactor is furnished with stirring means and has an overflow outlet located at a
 point which allows only five minutes'
 80 run of materials to be contained in the contactor. The mixture, only partially reacted in this time and containing mono-glycerides and diglycerides, passes from the outlet into a time coil or reactor of
 such dimensions that it takes about
 85 twenty-five minutes for the material to pass therethrough. During this period, the reaction proceeds to a point where two phases are present, and the mixture
 90 is then run into an acidification tank, where 2% sulphuric acid is added until a methyl red end point is reached; at this point, the pH is about 5. The acidified mixture is then run into a settling
 95 tank, where it is allowed to separate into two layers.

The lower glycerine layer is substantially continuously withdrawn at the
 100 bottom of the settling tank, and the upper layer overflows into a conduit through which it passes to a still. The excess alcohol is removed by distillation, and the bottoms from the still are run
 105 into a second settling tank, where a further amount of glycerine is settled out and withdrawn. The overflow from the second settling tank is divided into two
 portions. A first portion, substantially
 110 free of glycerine, is used without further distillation. The second portion is run into a vacuum distillation apparatus, where it is distilled at an absolute pressure of about 15 mm. of mercury. The
 115 methyl esters are topped from the still, and the bottoms or residue containing unreacted and partially reacted oil are continuously run back into the mixing vessel or contactor for reworking along with
 120 fresh oil.

EXAMPLE III.

215 parts by weight of coconut oil per
 minute is run into a contactor with 94
 parts per minute of ethyl alcohol contain-
 125 ing 2% by weight of sodium hydroxide. The contactor is of such dimensions that approximately ten minutes' run of material is contained therein, and the

overflow is connected with a reactor wherein the materials are turbulently agitated for some thirty minutes at the refluxing temperature. The effluent from the reactor passes into a mixer, and gaseous sulphur dioxide is introduced therein at a rate sufficient to neutralise the caustic and soap present. The acidified mass separates into two phases and flows to a settling tank, from which a lower glycerine layer is withdrawn at the bottom. The overflow from the tank is run into a still operated at atmospheric pressure. Excess ethyl alcohol is vaporised and removed, and the bottoms pass to a vacuum distillation apparatus. The ethyl esters and any remaining glycerine are topped off and separated in a second settling tank, and the distillation residue is run back into the reactor for reprocessing along with fresh coconut oil.

EXAMPLE IV.

285 parts by weight of cottonseed oil is mixed with 184 parts of ethyl alcohol and 1 part of concentrated sulphuric acid. The mixture is refluxed with stirring at the boiling-point of the ethanol for approximately an hour and is then neutralised with sodium acetate. Excess alcohol is volatilised off, and the distillation is continued under about 10 mm. absolute pressure. The distillate separates readily into two layers, a lower glycerine layer and an upper layer comprising the ethyl esters of cottonseed oil fatty acids.

EXAMPLE V.

A mixture of 143.4 grammes of tallow containing less than 1% by weight of moisture and 5% of the free fatty acids of tallow together with 80 grammes of methanol (an excess of about 400%) is heated with 1 gramme of sodium hydroxide to the reflux temperature of the methyl alcohol. The refluxing is continued for thirty minutes, and the reaction mixture is then neutralised to a pH of approximately 7.0 with about 15 cc. of glacial acetic acid. The neutralised mixture is heated over a steam bath to remove the excess methyl alcohol, and the mixture is then distilled under a reduced pressure equivalent to 10 mm. of mercury absolute. The distillate is allowed to stand, and a glycerine layer separates out and is withdrawn. A yield of distillate equivalent to about 96% of the calculated theoretical yield is obtained.

EXAMPLE VI

A mixture of 86 grammes of tallow and 48 grammes of methyl alcohol is heated with 0.65 gramme of sodium hydroxide

to the refluxing temperature of the alcohol for a period of a half hour. About 3.1 grammes of stearic acid is added to the reaction mixture to neutralise the catalyst, and excess alcohol is removed by heating on a steam bath. The entire residue is then distilled together at a pressure of about 10 mm. of mercury absolute. The distillate readily separates into an upper layer containing methyl esters of tallow fatty acids and a lower glycerine layer, and the distillate yield is more than 99% of the calculated theoretical yield.

EXAMPLE VII.

A mixture of about 860 grammes of tallow of a grade similar to that in Example V and 480 grammes of anhydrous methanol is heated with 6.5 grammes of anhydrous sodium hydroxide to the refluxing temperature of the methanol (i.e. about 64° C. to about 66° C.) for a period of approximately thirty minutes. The reaction mixture is then allowed to cool and to stand for three days. 1 gramme of stearic acid is then added to neutralise the sodium hydroxide which has not been used up in saponifying the methyl esters. Excess methyl alcohol is vaporised off, and the remainder of the reaction mixture is distilled. The distillate separates into two layers containing, respectively, esters and glycerine.

EXAMPLE VIII.

About 100 parts by weight per minute of coconut oil is mixed with 72 parts per minute of methanol and 1 part per minute of concentrated sulphuric acid. The mixture is run into a reaction coil having a holding time of some forty-five minutes and is there heated to a temperature of approximately 135° C. under sufficient pressure to maintain a liquid methanol phase. The effluent passes through a mixing coil where a stream of alcoholic sodium hydroxide is added at a rate just insufficient to neutralise the reaction mixture. The neutralisation is then completed by introducing a stream of an alcoholic solution of a sodium coconut oil soap at a sufficient rate to accomplish the neutralisation. The neutralised mixture flows into a column still, where excess alcohol therein is topped off, and the bottoms pass over steam coils at the bottom of the still which serve as a reboiler. The temperature of the residue is raised therein to about 140° C., and it is flashed into a vaporisation chamber maintained at about 135° C. and under a reduced pressure of 10 mm. of mercury absolute. The distillate is collected and

separates into a lower glycerine layer and an upper layer containing the methyl esters.

EXAMPLE IX.

5 285 parts by weight per minute of tallow is preheated to 130° C. and is passed through a homogeniser together with 300 parts of glycerine at about the same temperature. Concentrated sulphuric acid is introduced into the homogeniser at a rate of 1 part per minute. The effluent from the homogeniser is run into a reaction coil having a holding time of about thirty minutes, a temperature of 130° C. being maintained, and the reaction mixture therefrom passes into a mixing coil. Sodium hydroxide dissolved in glycerine is there added to the mixture at a rate just insufficient to neutralise the reaction mixture, and the mixture flows into a continuous vacuum still maintained at a pressure of about 4 mm. of mercury absolute. Glycerine is distilled off at about 150° C., and the remainder of the mixture comprising tallow fatty acid monoglycerides is continuously removed and collected.

EXAMPLE X.

An amount of cottonseed oil is mixed with twice its weight of propylene glycol and about 0.4% of its weight of concentrated sulphuric acid. The mixture is heated to 140° C. and is kept at this temperature for about three hours. Sodium hydroxide is then added in amount just insufficient to neutralise the mixture. The mixture is thereafter distilled at an absolute pressure of 3 to 4 mm. of mercury. Cottonseed fatty acid monoesters of propylene glycol are distilled off between 170° C. and 180° C., and a yield of monoesters equivalent to approximately 90% of the calculated theoretical yield is obtained.

EXAMPLE XI.

45 Equal weights of tallow and glycerine are mixed together and heated to about 180° C. Sodium hydroxide is then added intermittently to the total amount of about 0.5% of the weight of the tallow over a period of some three hours. During this time the temperature is maintained between 210° C. and 220° C. at atmospheric pressure, and an atmosphere of carbon dioxide is provided. The mixture is cooled and transferred to a separatory vessel, and glycerine settles out and is withdrawn. An amount of glacial acetic acid about three times the weight of sodium hydroxide employed is added to the upper layer, and it is taken up with some 3 to 4 volumes of ether, is repeatedly

washed with water, is dried and is blown to remove ether. The material is put in a distillation vessel and boils at about 230° C. to about 240° C. under an absolute pressure of 1 to 2 mm. of mercury. A distillate comprising tallow fatty acid mono-glycerides is collected, and a yield of distillate approximating 87% of the calculated theoretical yield is obtained.

The ester fractions obtained by alcoholysis of natural fatty acid glycerides according to the present invention, with or without washing and/or subsequent purification, can be employed in many chemical processes and products, as in the paint, perfumery, lubricating oils, medicinals and other fields. They may be used in many chemical syntheses and reactions and one of their greatest outlets for volume consumption is in the soap-making industry.

In our co-pending application No. 16960/43 (Serial No. 578,751) a process for the alcoholysis of fatty glycerides containing free fatty acids is claimed in which the free fatty acids are removed by first treating the fatty glycerides with an alcohol solvent for the free fatty acids at least partially immiscible with the fatty glycerides and separating the alcohol containing the free fatty acid before the alcoholysis reaction. The free fatty acid in the alcohol phase is then reacted with the alcohol solvent by adding a catalyst thereto, the said catalyst being an acid catalyst when an alkaline catalyst is used for the main alcoholysis reaction and *vice versa* and the alkyl esters being then added to the reaction mixture from the main alcoholysis reaction whereby the catalyst therein is partly neutralised, complete neutralisation being afterwards effected. No claim is made to this process herein.

In our co-pending application No. 3828/44 (Serial No. 587,533) a process is claimed for the alcoholysis of fatty glycerides with an aliphatic mono-hydric alcohol having one to six carbon atoms per molecule in the presence of a catalyst at a temperature above the normal boiling point of the alcohol and a pressure sufficient to maintain a liquid alcohol phase. No claim is made herein to this process *per se*.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that subject to the above disclaimers what we claim is:—

1. A process for the alcoholysis of fatty glycerides which comprises reacting the said glycerides and an alcohol in the presence of an alcoholysis catalyst in

which the free alcohol reaction component is a monohydric or a polyhydric alcohol, characterised in that before removing unreacted alcohol and recovering the reaction products from the liquid reaction mixture the influence of the catalyst is removed by the addition of a neutralising agent.

2. A process as claimed in Claim 1 wherein the reaction products are recovered by distillation.

3. A process as claimed in Claim 1 or Claim 2 wherein the alcohol employed for alcoholysis is an aliphatic monohydric alcohol having 1 to 6 carbon atoms whereby alkyl esters and polyhydric alcohol are obtained.

4. A process as claimed in Claim 1 or Claim 2 wherein the alcohol employed for alcoholysis is a polyhydric alcohol having two to six carbon atoms whereby partial esters of polyhydric alcohols are obtained.

5. A process as claimed in Claim 3 wherein the alcoholysis is carried only to the point where mono- or di-esters of glycerine are formed whereupon additional monohydric alcohol or catalyst is added.

6. A process for the alcoholysis of fatty glycerides of the type described which comprises reacting a fatty glyceride with a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an alkaline alcoholysis catalyst to provide a liquid body containing alkyl esters, glycerine and unreacted alcohol, adding sufficient acidic material to the liquid body to obtain a pH of about 5 to about 7, volatilising unreacted alcohol from said liquid body to leave an upper layer containing alkyl esters and a lower layer containing glycerine, and separating the upper layer from the lower layer.

7. A process for the alcoholysis of fatty glycerides of the type described which comprises reacting a fatty glyceride with a saturated, aliphatic, monohydric alcohol having one to about six carbon atoms per molecule in the presence of an acid alcoholysis catalyst to provide a liquid body containing alkyl esters, glycerine and unreacted alcohol, adding sufficient alkaline material to the liquid body to give a pH of about 5 to about 7, volatilising unreacted alcohol from said liquid body, and distilling the remainder of the liquid body under reduced pressure to obtain a distillate comprising alkyl esters and glycerine, whereby said esters and glycerine can be readily separated.

8. A process for preparing fatty acid monoesters of glycerine by alcoholysis of fatty glycerides which comprises reacting a glyceride of a fatty acid having about twelve to about twenty carbon atoms per molecule of fatty acid with an excess of glycerine in the presence of an alcoholysis catalyst to provide a liquid body containing a fatty acid monoglyceride and unreacted glycerine, bringing the liquid body to a pH of about 5 to about 8, and recovering said unreacted glycerine and said fatty acid monoglyceride.

9. A process as claimed in Claim 8 wherein the glycerine and fatty acid monoester are recovered by distillation under reduced pressure.

10. A process for the alcoholysis of fatty acid esters substantially as described in any one of the specific examples herein.

11. Alkyl esters, partial esters of polyhydric alcohols and mono- or polyhydric alcohols whenever produced and recovered in the alcoholysis process as claimed in any one of the preceding claims.

Dated this 16th day of February, 1944.

KILBURN & STRODE,
Agents for the Applicants.

Printed for His Majesty's Stationery Office, by M.M.P. Ltd.—1948

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.